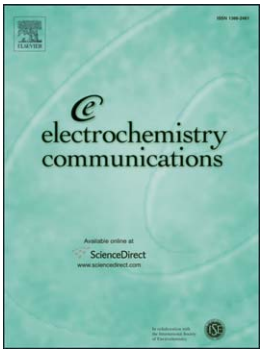

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Carbon-supported shape-controlled Pt nanoparticle electrocatalysts for direct alcohol fuel cells

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Abstract:

The demand for power sources alternative to fossil fuels makes urgent the development of more efficient electrocatalysts for fuel cells applications and the maximization of the performances of the existent ones. This work reports, for the first time, the use of carbon-supported shape-controlled Pt nanoparticles as anode catalysts in direct ethanol fuel cells. By using cubic Pt nanoparticles, on which (100) surface sites are predominant, the performance of the fuel cell can be increased from 14 to 24 mW per mg of Pt when compared with cuboctahedral nanoparticles. Moreover, the open circuit potential shifts about 50 mV toward more positive potentials. In comparison with commercially available Pt catalysts, the performance for the (100) preferentially oriented nanoparticles is about 3 times higher. The reported results evidence that, from an applied point of view, the effect of the surface structure/shape of the electrocatalysts can be also considered to improve the performance of real fuel cell systems.

Keywords: direct ethanol fuel cells, shape controlled nanoparticles, electrocatalysis

1. Introduction:

Direct ethanol fuel cells (DEFC) have emerged in the last years as a promising alternatives as energy sources for portable applications because ethanol is easier to store/transport and safer to handle than the "traditional" hydrogen fuel [1]. When compared with other alcohol fuels such as methanol [2], ethanol has several advantages, such as low toxicity, higher theoretical energy content and the fact that it can be produced in large scale from biowaste [3].

The major drawback in the commercialization of DEFCs is its still low performance caused by the incomplete oxidation of ethanol on the anode side. Platinum is considered one of the best catalysts for ethanol oxidation [4] (and many other small organic molecules [5]) although it can be poisoned at low potentials with reaction intermediates, such as CO, thus blocking the catalyst surface and impeding the reaction to proceed.

One of the key factors controlling the activity and selectivity of Pt is its surface structure [6, 7]. Studies performed with Pt single crystals show that changing the surface orientation affects the reactivity of the surface toward ethanol oxidation [8, 9]. In addition, it is known that by tuning the shape of the Pt nanoparticles, the desired surface orientation can be achieved [10]. For instance, cubic Pt nanoparticles are ideally enclosed by six (100) facets while, in contrast, cuboctahedral particles contain both (100) and (111) facets [10]. In this way, the most favorable surface sites for a certain reaction can be preferentially obtained in the catalyst in order to maximize the activity. Shape-controlled Pt nanoparticles (nanoparticles where the shape has been designed to increase the presence of certain surface site) have been studied for ethanol oxidation [11] under electrochemical conditions without carbon support. It has been shown that in nanoparticles with higher amount of (111) sites, the main product of ethanol oxidation is acetic acid, and the amount of CO_2 produced is negligible, while (100) preferentially oriented Pt nanoparticles are more effective for the cleavage of the C–C bond yielding adsorbed CO, which eventually is oxidized to CO_2 [11]. Despite higher activity of cubic Pt nanoparticles has been reported, there are no studies of carbon-supported shape-controlled Pt nanoparticles for direct ethanol fuel cell measurements and the only fuel cell results reported are concerned with hydrogen fuel cells [12].

In this work, carbon-supported (100) preferentially oriented Pt nanoparticles were evaluated as anode catalyst for DEFC. For sake of comparison, commercial and home-made cuboctahedral Pt were also tested under similar fuel cell conditions. The results indicate that changing the shape of the nanoparticles, the performance of the DEFC can be increased.

2. Experimental:

The polycrystalline and (100) preferentially oriented Pt nanoparticles used in this study were prepared by the water in oil microemulsion method as described previously [13]. Specific amounts of carbon powder (Vulcan-XC-72R, Cabot Corp.) were added to each micellar solution to achieve a final metal loading of 20%. Commercially available Pt nanoparticles (Pt 20% on Vulcan from Alfa Aesar) were also used for comparison.

The fuel cell experiments were performed at 70 ºC in a single cell DAFC with a surface area of 5.29 cm^2 [14]. An aqueous 1 M ethanol (Altia p.a.) solution was fed to the anode (Pt poly, Pt (100) or Pt comm) with 1.5 ml min^{-1} rate and humidified oxygen gas (5.0 Aga) to the cathode (Pt 60 % on Vulcan from Alfa Aesar) at 200 ml min^{-1}. The cell was stabilized overnight (0.2 ml min^{-1}) and normalized 1 h prior to the experiments with the higher flow rates. Membrane electrode assemblies (MEAs) of the three catalyst materials were prepared by painting an ink made from the catalyst, Nafion® ionomer dispersed in aliphatic alcohols (Aldrich) and isopropanol (Merck, p.a.) on a Nafion® 115 (Dupont) membrane with an airbrush (Badger, model 100). Before use, the MEA was dried in a vacuum oven for 2 h and heat pressed at 130°C, with 50 kN pressure for 120 s. The Pt loading on the MEAs was 0.66 ± 0.01 mg cm^{-2} for the anode and 2.0 ± 0.2 mg cm^{-2} for the cathode. Higher loading on the cathode were used to avoid limitations on the fuel cell performance due to the oxygen reduction. The fuel cell was assembled with PTFE gaskets, diffusion layers (carbon cloths, Ludlow Coated products) and the MEA, closed and tightened evenly with 10 kN force [14].

The electrochemical measurements were performed with an Autolab PGSTAT 20 instrument equipped with an Autolab BSTR10A booster controlled by GPES software (version 4.9 by Eco Chemie B.V.). The polarization curves were measured with a scan rate of 0.5 mV s^{-1} and the obtained currents were normalized to the catalyst mass.

All the catalysts were characterized using X-ray diffraction (XRD - PanAnalytical X'Pert Pro) and High-resolution transmission electron microscopy (HRTEM - double-aberration-corrected JEOL 2200FS microscope equipped with a field emission gun operating at 200kV).

3. Results and discussion:

In this work, three Pt catalysts were tested as DEFC anodes – Pt cuboctahedral (Pt_{poly}), cubic nanoparticles ($Pt_{(100)}$) and Pt catalyst commercially available (Pt_{comm}). Prior to the measurements, the nanoparticles were analyzed by XRD and HRTEM to analyze their size and shape. The obtained results are presented in Figure 1.

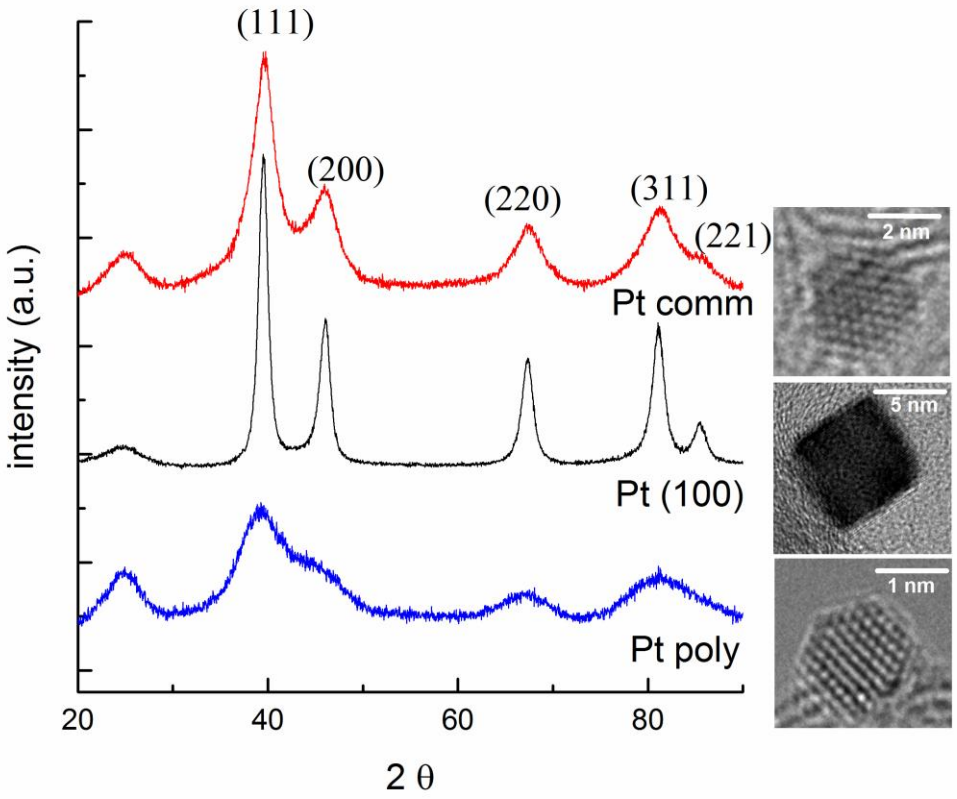

Figure 1 - XRD diffractograms and respective HRTEM images of the anode catalysts.

The XRD diffractograms of the catalysts show different peak broadening as a consequence of the different size of the nanoparticles, suggesting that $Pt_{(100)}$ are the largest ones (sharper peaks) and the Pt_{poly} the smallest (broader peaks). Five main peaks were observed in all the samples and were assigned to a face-centered-cubic (fcc) crystal phase of Pt. Thus, peaks at 2θ positions - 39.6°, 45.7°, 67.6°, 81.1° and 85.5° - corresponding to (111), (200), (220), (311) and (221) crystallographic planes [15] (JCPDS card 01-087-0647), respectively were clearly identified. An additional peak at 25.0° is due to the carbon support (Vulcan) of the catalyst. The analysis of the XRD and HRTEM revealed that the particles size is 2.7 nm for the Pt_{comm}, 1.6 nm for Pt_{poly} and 6.7 nm for $Pt_{(100)}$ as suggested by the different width of the peaks in the diffractograms. The HRTEM images show that both commercial and Pt_{poly} nanoparticles have cuboctahedral shape, constituted mainly by (111) and (110) facets. The shape of the $Pt_{(100)}$ nanoparticles is cubic, as expected for this kind of structures [6].

Pt nanoparticles with different shape, and consequently different surface orientation show significant differences on their voltammetric profile. To complete the physical characterization of the catalysts used in this study, cyclic voltammograms in 0.5 M H_2SO_4 were performed (inset in Figure 2A). The results show that the "home-made" nanoparticles present sharper and better defined adsorption states in the hydrogen region than the commercial ones, which is known to be related with a higher level of surface cleanness.

The main voltammetric features identified in the CVs are the peaks centered at 0.125, 0.27 and 0.35-0.37 V [6, 16]. The first two contributions are present in all the nanoparticle samples and correspond to (110)-type sites (peak at 0.125 V) and to the presence of (100) defects on (111) domains and (100) short domains (peak at 0.27). Those are typically the only contributions typically observed for Pt samples with no preferential surface orientation (Pt_{comm} and Pt_{poly}). When the surface structure presents a preferential orientation ($Pt_{(100)}$), the peak at 0.35-0.37 V is observed due to the presence of (100)

ordered domains. All these voltammetric profiles agree with those expected from the HRTEM measurements, which reflect the surface structure-particle shape correlations.

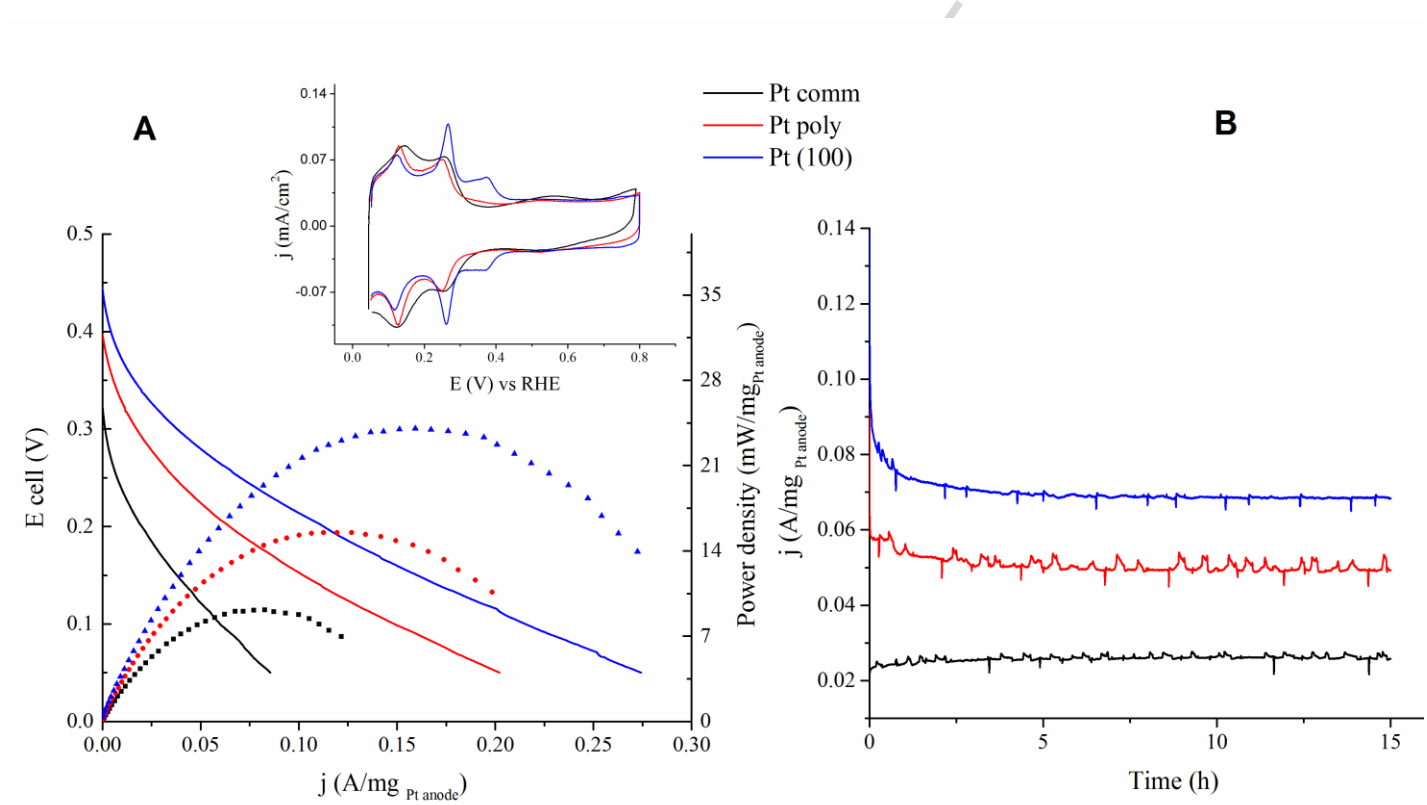

Figure 2 – A) Polarization and power density curves and B) Chronoamperometry curves at 0.2 V obtained for Pt_{comm}, Pt_{poly} and $Pt_{(100)}$ as anode catalysts obtained from the fuel cell measurements at 70 ^{o}C, with 1 M ethanol as fuel and 200 ml/min O_2 as oxidant. Inset: Cyclic voltammograms for Pt_{comm}, Pt_{poly} and $Pt_{(100)}$ in 0.5 M H_2SO_4, 50mV/s.

DEFC experiments were performed for three MEAs containing Pt_{comm}, Pt_{poly} and $Pt_{(100)}$ catalysts as anode electrodes (Figure 2A). For the evaluation of the catalyst polarization curves were measured and the corresponding power density curves calculated. The results show that the single cell performance is clearly dependent on the used Pt nanoparticles and consequently on their particular particle shape/surface structure.

The Pt_{comm} presents the lowest performance within the three Pt nanoparticles studied. The current density at 0.2 V is 0.03 $mA/mg_{Ptanode}$ catalyst while for Pt cubic nanoparticles (showing the best performance) is 0.11 $mA/mg_{Ptanode}$ catalyst. When comparing the Pt_{comm} and Pt_{poly}, and despite both are cuboctahedral with (111) and (100) facets as observed by HRTEM (Figure 1), they display however, a different performance. While the maximum power for the Pt_{poly} sample is 15.51 mW/ $mg_{Ptanode}$ catalyst, for the Pt_{comm} sample is only 9.11 mA/ $mg_{Ptanode}$. The XRD and HRTEM results (Figure 1) show that the mean size of the particles is different, being that of the "home-made" synthesized particles smaller. Thus, the differences between the fuel cell performance for the two cuboctahedral nanoparticles can result from a surface area effect because the smaller particles have higher surface area for the same amount of catalyst. However, taking into account the shape of the CV and the definition of the hydrogen adsorption/desorption peaks, in addition to the surface area, the cleanness of the particles can also have a great influence on the performance of the fuel cell. The $Pt_{(100)}$ nanoparticles are, within the studied catalysts those displaying the best fuel cell performance. The maximum power density (24.0 $mW/mg_{Ptanode}$ catalyst) is obtained at 50 mV lower potential than with the commercial sample and the open circuit potential (OCP) is the highest (~440 mV) from all the studied anodes. These results are in good agreement with previous electrochemical studies on the influence of the surface structure on ethanol oxidation with single crystals and non-supported shape controlled nanoparticles [8, 9, 11, 17]. Thus, nanoparticles with a large fraction of (100) surface sites showed higher current densities for ethanol oxidation at higher potentials (above 0.6-0.7 V vs RHE) [11]. This behavior reflects the ability of the (100) sites to catalyze the C-C bond cleavage from ethanol at low potentials. However, the bond breaking has as major product CO [18] that blocks the surface activity at lower potentials due to the formation of full coverage layer on the surface, and the activity is only recovered when CO is oxidized (> 0.7 V vs RHE which corresponds to low cell voltages). For an easier comparison of the results obtained with single crystal electrodes and those obtained under fuel cell conditions, we should keep in

mind that, concerning the potential scale, low potentials in electrochemical cell correspond to high cell voltages (and vice versa). The higher activity from (100) Pt sites toward C-C bond cleavage has been attributed to its surface coordination, which favors the initial dehydrogenation of ethanol due to its ability to adsorb C-containing fragments and then oxidize CH_3O species (see [19] and references therein). For potential regions lower than 0.6 V (vs RHE), the highest current densities are obtained with (111) preferential oriented nanoparticles which also shown the lowest onset potential. Finally, nanoparticles with intermediate amounts of (100) sites (like Pt_{comm} or Pt_{poly} used in this study) show intermediate activities [11].

Looking into our results under these observations, we can observe that the catalytic effect at higher potentials from the (100) sites is also observed in the fuel cell performance as $Pt_{(100)}$ catalyst presents higher current densities at low cell voltages (high anode potentials). However, it would be expected that polyoriented samples would have a higher OCP as reflected by the lowest onset potential in the electrochemical experiments. Yet, that is not the case and in addition to the higher current densities at lower cell voltages, $Pt_{(100)}$ also shows the highest value for the OCP. This effect is most likely due the higher activity of these surface sites toward C-C bond cleavage at the lower anode potentials (higher cell voltages) that has CO as main reaction product. However, the high operating temperatures (70º C) of the fuel cell will favor the CO oxidation [20] minimizing the CO poisoning effect under these conditions. In this way, $Pt_{(100)}$ higher activity toward C-C bond breaking leads to better fuel cell performances. In addition, mass transfer limitations existing in electrochemical cells are less pronounced under constant flow of ethanol and the higher temperature of the fuel cell (70 ºC) can also lead to differences in performance. These effects can explain the best overall performance observed for the $Pt_{(100)}$ catalysts in fuel cell conditions.

The stability of the catalysts over time was evaluated with chronoamperometric experiments during 15 h at a constant cell potential of 0.2 V and the results obtained are shown in figure 2B. As expected from the polarization curves, the catalyst presenting the highest current densities in the chronoamperograms is $Pt_{(100)}$. Both "home-made" catalysts show a decrease on the measured currents in the first 2.5 hours. This can be due to the formation of some adsorbed species on the catalyst layer from oxidation reaction [21]. The Pt_{comm} shows an opposite behavior immediately after starting the measurements. Its activity increases during the first 2 hours suggesting that, the surface is being electrochemically activated. Based on the CVs presented as insets in Figure 2, the commercial catalyst surface seems to be less clean than the "home-made" catalysts. In any case, both cuboctahedral and cubic nanoparticles show good stability during the 15 hour measurement. It should be mentioned that polarization curves were obtained for all the catalysts after the chronoamperometric measurements. These polarization curves were essentially identical to the initial ones (results not shown), suggesting that no significant changes on the nanoparticles occurred during the measurements.

The obtained results clearly indicate that the optimization of the surface structure/shape of the Pt electrocatalysts allow important improvements of the fuel cell performance to be achieved. However, it is also well-established that the state-of-the-art catalysts for DEFC are no longer pure Pt but multimetallic (bi, tri or even more) Pt-based catalysts [22]. In fact, maximum power densities of about 100 mW/cm^2 have been already reported using Pt alloy nanoparticles [23, 24]. These maximum power densities are much higher than that here reported (about 16 mW/cm^2). However, this value strongly depends on Pt metal loading and therefore, a more appropriate comparison must be made by using the *maximum mass specific power density* which accounts the maximum power density per total mg of Pt (anode + cathode) catalyst [22] . In this case, a reasonably good value of 0.03 $mW/\mu g_{Pt}$ is obtained in comparison with the state-of-the-art which is about 0.05 $mW/\mu g_{Pt}$. Therefore, this contribution may be

considered an starting point on the use of shape-controlled Pt nanoparticles for DEFCs from which further improvements would be expected by using different and well established strategies such as the employ of adatoms decorated (Sn, Ru, Rh and their possible combinations) shape controlled Pt nanoparticles or even the development and use of shaped Pt alloy (PtSn, PtRu, PtRh, PtRuSn,…) nanoparticles.

4. Conclusions:

This work reports, for the first time, the use of shape-controlled nanoparticles as anodes for DEFC. The results show that by using cubic Pt nanoparticles, where (100) surface sites are predominant, the performance of the fuel cell can be increased from 14 to 24 $mW/mg_{Ptanode}$ catalyst when compared with cuboctahedral Pt. Moreover, the OCP shifts about 50mV toward more positive potentials. If the comparison is done with commercially available Pt catalysts, the obtained performance is 3 times higher for the preferentially oriented (100) nanoparticles. The highest activity of (100) surface domains toward C-C bond breaking from ethanol is also observed in fuel cell conditions leading to higher fuel cell performances with good stability over 15 hours of measurements.

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Highlights

- Carbon-supported shape-controlled Pt nanoparticles were tested as DEFC anodes
- Pt nanoparticles with more (100) surface sites showed increased performance
- Pt(100) nanoparticles presented 50 mV higher OCP
- The ability of (100) sites to break C-C bonds from ethanol was observed in DEFC